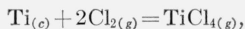


Heat of Formation of Titanium Tetrachloride

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The heat of formation of gaseous titanium tetrachloride has been measured by the reaction of metallic titanium with gaseous chlorine in a calorimeter. The value for the heat of formation obtained in this investigation corresponds to the reaction:



$$\Delta H_f^\circ(25^\circ \text{C}) = -763.2 \pm 2.9 \text{ kJ/mole } (-182.4 \pm 0.7 \text{ kcal/mole}).$$

Earlier data are discussed briefly.

1. Introduction

This investigation is part of a program on the determination of the thermodynamic properties of titanium compounds sponsored by the Office of Naval Research; it is also a part of the work of the thermochemical laboratory of the Bureau on the determination of the heats of formation of compounds of importance to science and industry.

The heat of formation of TiCl_4 may be obtained by several different methods, each having certain advantages and disadvantages. Titanium tetrachloride hydrolyzes rapidly in water forming aqueous hydrochloric acid and titanium dioxide; under these conditions, however, it is difficult to determine the thermodynamic state of the precipitated TiO_2 . Metallic titanium will react at room temperature with liquid chlorine, or with chlorine gas under pressure to form the tetrachloride. In either case, the observed heat of reaction is complicated by the mutual heats of solution and vaporization of the tetrachloride and chlorine.

Metallic titanium reacts rapidly with an excess of chlorine under atmospheric pressure at about 300°C to produce gaseous TiCl_4 . In this case there is no uncertainty regarding the thermodynamic state of the reactants and products and the process is well defined. It is necessary, however, to measure accurately the fairly large amount of energy required to maintain the reaction temperature. Since the uncertainty in this measurement can be evaluated quite accurately, the direct reaction between metallic titanium and gaseous chlorine was selected for measurement.

2. Source and Purity of Materials

The titanium sample was obtained by reduction of the iodide and was supplied by the Naval Research Laboratory (courtesy of E. J. Chapin). This sample was taken from material for which the purity was stated to be in excess of 99.99 percent.

The chlorine was obtained from the Matheson Company. The gas phase existing at the boiling point of liquid nitrogen was analyzed by means of the mass spectrometer by Shuford Schuhmann of the Gas Chemistry Section of the Chemistry Division.

The following results were obtained in volume percent: H_2 , 0.00; CO , 0.00; $(\text{N}_2 + \text{O}_2 + \text{A})$, 0.01. The purity of a second sample was determined to be 99.99 mole percent from cryoscopic measurements by Gaylon S. Ross of the Pure Substances Section of the Chemistry Division.

A sample of the helium, taken directly from the cylinder, was found to contain less than 0.01 percent of oxygen and nitrogen from an analysis by Vernon H. Dibeler of the Mass Spectrometry Section of the Atomic and Radiation Physics Division.

3. Apparatus

The glass reaction vessel (fig. 1) consisted of a quartz tube, closed at the bottom, upon which was wound a 139-ohm manganin heating coil, surrounded by a vacuum jacket. The jacket was silvered on the inside to reduce the amount of energy transferred by radiation. The sample was placed in a quartz crucible on the bottom of the quartz tube. Chlorine was admitted through a centrally located quartz inlet tube that extended down into the crucible so that the gas was directed against the hot sample. The exit gases passed out through a glass helix in which they were cooled to the temperature of the calorimeter.

The calorimeter was of the isothermal jacket type similar to that described previously [1]¹ except that a smaller calorimeter can and well were used, which resulted in a considerably lower energy equivalent. The temperature of the calorimeter jacket was maintained constant at 27°C within $\pm 0.001^\circ \text{C}$. The thermometric system and the apparatus for measurement of electrical energy have been described in a previous report [2]; all equipment was calibrated in terms of standards maintained at the Bureau.

The gas train used in these experiments is shown in figure 2. The helium was passed successively through heaters containing sponge titanium and copper oxide at 600°C and through absorbers containing Ascarite, magnesium perchlorate, and phosphorus pentoxide. The chlorine was dried by passing it through an absorber containing phosphorus pentoxide. Valves were provided whereby either

¹ Figures in brackets indicate the literature references at the end of this paper.

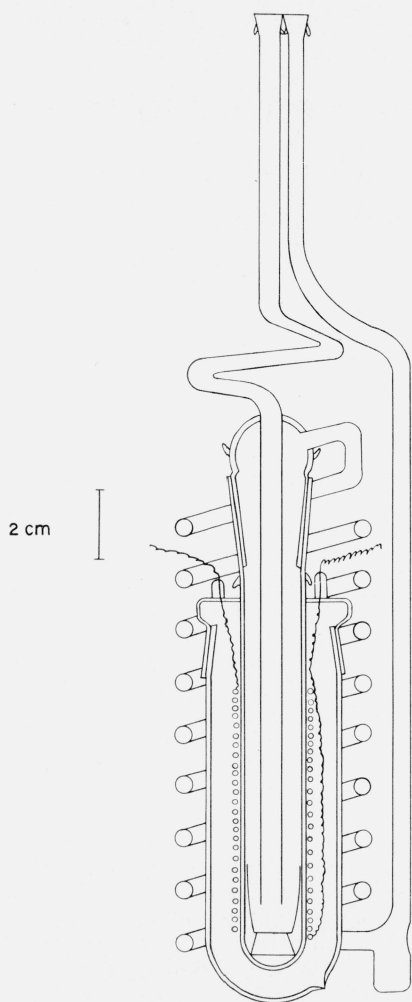


FIGURE 1. Reaction vessel.

the helium or the chlorine could bypass the calorimetric vessel. The exit gases were passed through a trap cooled with liquid nitrogen to collect the excess chlorine and the titanium tetrachloride vaporized during the experiment.

4. Procedure

A sample (0.2 to 0.4 g) of titanium was weighed into the quartz crucible and the vessel assembled and placed in the calorimeter can with 1,855 g of water. The air and moisture were removed as completely as possible from the vessel by successive evacuation and filling with purified helium.

The calorimetric temperature observations were divided into three periods, a 60-min reaction period and two 20-min rating periods, one immediately preceding and the other following the reaction period. Temperatures were observed at 1-min intervals during the reaction period and at 2-min intervals during the rating periods [3].

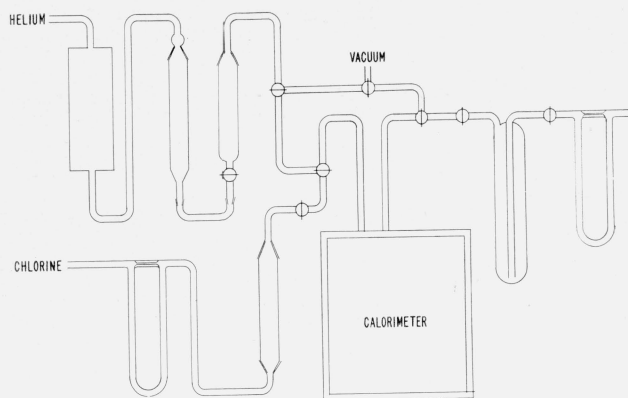


FIGURE 2. Gas train.

Chlorine was introduced into the vessel at the start of the reaction period, and the vessel was heated electrically. When the desired rise in temperature was obtained, the electric current was interrupted, the flow of chlorine stopped, and helium was introduced into the vessel to flush out the remaining chlorine. The helium was allowed to flow for about 30 min and then stopped. An additional 10 min was allowed for thermal equilibrium to be re-established, after which temperatures were observed during the final rating period.

The rates of flow of chlorine and helium were determined by means of calibrated capillary flowmeters; the total quantities were determined from the rate and time of flow. The temperature of the helium and chlorine was assumed to be the same as that of the calorimeter jacket through which they passed. These data were required only for calculation of the small correction for the heat carried into the calorimeter by the chlorine and helium.

The quantity of reaction was determined from the mass of sample, since the reaction was complete in all cases. The liquid TiCl_4 remaining in the vessel was flushed out with helium and the quantity determined by analysis [4]. These data were used to correct the results for the heat of vaporization of the portion of the liquid that did not vaporize during the experiment. The contents of the trap were also analyzed for TiCl_4 ; this served as a check on the amount of reaction.

After all the TiCl_4 was flushed out, the vessel was disassembled, and the crucible was removed and weighed. No correction was made for the very slight residue, the mass of which was always less than 1 mg.

The calorimetric system was calibrated in exactly the same manner except for omission of the titanium and chlorine. In each case the quantity of electrical energy was carefully measured and the initial and final temperatures of the calorimeter reproduced as closely as possible. This is known as the substitution method of calorimetry, in which the energy associated with a known quantity of a given chemical reaction is directly compared with electrical energy in terms of calibrated standards.

5. Results and Calculations

The results of the electrical calibration experiments are given in table 1, in which E_e is the electrical energy added to the system, ΔRc is the corrected temperature rise expressed in ohms, q_g is a correction to 25° C for the heat capacity of the helium, and E_s is the energy equivalent of the system in joules per ohm.

The results of the calorimetric experiments are given in table 2. The quantity q is the total energy absorbed by the calorimeter, obtained as the product of E_s and ΔRc . The apparent heat of the chemical reaction, q_r , is obtained as the difference between q and E_e . The quantity q_g is a correction to 25° C for the heat capacities of the reactants, products, and the helium; the quantity q_v is a correction for the vaporization of the titanium tetrachloride remaining in the vessel after the experiment.

TABLE 1. Results of the electrical calibration experiments

Experiment No.	E_e	q_g	ΔRc	E_s
	j	j	<i>Ohm</i>	<i>j/ohm</i>
1.....	29564.8	20.1	0.354054	83560.4
2.....	29343.7	18.7	.351368	83565.9
3.....	28454.1	19.2	.340776	83554.3
4.....	29161.9	11.1	.349191	83544.8
5.....	28043.6	9.7	.335833	83533.5
Mean.....				83551.8
Standard deviation of mean.....				±5.8

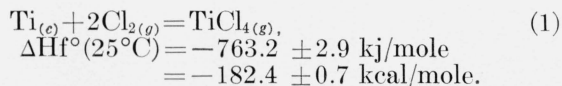
TABLE 2. Results of the calorimetric experiments on titanium tetrachloride

Experiment No.	ΔRc	q	E_e	q_r	q_g	q_v	Ti	$-\Delta H(25^\circ C)$
	<i>Ohm</i>	j	j	j	j	j	<i>Moles</i>	<i>kJ/mole</i>
1.....	0.329287	27512.5	24432.2	3080.3	-9.5	-38.5	0.0039944	759.14
2.....	.363176	30344.0	27562.4	2781.6	-8.5	-25.1	.0035962	764.14
3.....	.399533	33381.7	29497.0	3884.7	-2.1	-48.8	.0049891	768.44
4.....	.348517	29119.2	25262.4	3856.8	-7.3	-77.0	.0049418	763.39
5.....	.345635	28878.4	26180.8	2697.6	-10.7	-24.9	.0034975	761.12
6.....	.352348	29439.3	24309.2	5130.1	-7.7	-158.4	.0065039	763.23
Mean.....								763.24
Standard deviation of mean.....								±1.28

The heat of vaporization of titanium tetrachloride was taken as 9.9 kcal/mole from the calorimetric measurements of Schaffer, Breil, and Pfeffer [5]. The density of titanium was taken as 4.50 g/cm³ [6]. The heat of reaction obtained in joules per mole was converted to the conventional thermochemical calorie by the following relationship:

$$1 \text{ cal} = 4.1840 \text{ j.}$$

The mean value for the heat of formation given in table 2 corresponds to the following reaction:

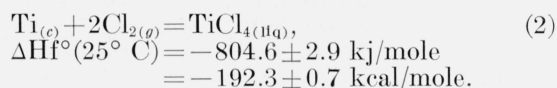


Another series of five experiments was performed on samples taken from a sheet of commercial titanium obtained from the Titanium Metals Corporation of America. The manufacturer furnished the following analyses in percent: Ti, 99.74; C, 0.019; N₂, 0.047; Fe, 0.08; and O₂, 0.17. The heat of formation corresponding to reaction (1) obtained for samples from this sheet was -764.0 ± 2.1 kJ/mole (-182.6 ± 0.7 kcal/mole).

A single experiment was also carried out using a sample of sponge titanium obtained from the Bureau of Mines (courtesy of David Schlain). The heat of formation obtained was -763.6 kJ/mole (-182.5 kcal/mole).

The uncertainties assigned to the values given in this paper were obtained by combining twice the standard deviation of the mean of the calibration and reaction experiments with reasonable estimates of all other known sources of error.

Combination of (1) with the heat of vaporization of TiCl₄, 9.9 kcal/mole, gives the heat of formation of liquid TiCl₄.



6. Discussion

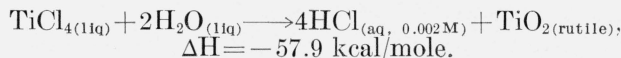
After vaporization of the liquid titanium tetrachloride from the vessel, there was usually a very small, reddish deposit remaining in the bulb of the vessel. This material was nonvolatile and was soluble in the liquid tetrachloride. It was not possible to remove any of this material because of its small quantity and its tendency to adhere to the vessel. It was, therefore, dissolved by washing with 5 percent sulfuric acid and the quantity determined by analysis. The quantity of Ti was found to be not more than 0.25 percent of the original sample. Although the composition of the substance is not known, the titanium present has been assumed to be in the form of an oxide or an oxychloride of titanium. The heat of formation of titanium dioxide is -225.7 kcal/mole [7] and that of TiOCl₂ has been estimated to be -205 kcal/mole. In view of this information it would appear that the maximum error in the heat of formation of TiCl₄ caused by production of this material would be less than 0.1 kcal/mole which is well within the uncertainty ascribed to the value given in this paper.

Two samples of the TiCl₄ produced in the reaction were examined by means of the mass spectrometer. The analyses showed that the material was free from SiCl₄ but contained some of the fluorocarbon stopcock grease. There was no evidence of reaction between the grease and the TiCl₄ vapors; it appears, however, that liquid TiCl₄ reacts slowly with the grease resulting in the displacement of one or more chlorine atoms with fluorine. There was no contact of liquid TiCl₄ with the grease in the calorimeter; the contact was made during the analysis.

The emission spectrograph analysis of one of the

samples of TiCl_4 obtained from the commercial titanium gave 0.0015 percent Si, 0.0010 percent Ni, 0.0005 percent Sn, 0.0005 percent Al, and a total of 0.0009 percent of other metals. This analysis was performed by Martha Mayo Darr of the Spectrochemistry Section of the Chemistry Division. If these impurities are assumed to be present as chlorides, the error in the measured heat of formation due to these materials would amount to less than 0.01 percent.

Prior to this investigation, calculations of the heat of formation of TiCl_4 were based on the experimental data obtained by Thomsen for the heat of hydrolysis [8]. He reported the results obtained for the following reaction at 18°C :



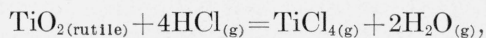
Thomsen reported that when the HCl produced in the reaction was titrated with NaOH only 47.7 kcal was evolved instead of the 55.0 to be expected from the neutralization of 4 moles of dilute NaOH at 18°C . This has caused considerable confusion in the use and interpretation of his results.

From Thomsen's data Roth and Becker [9] calculated the heat of formation of liquid TiCl_4 to be -185 kcal/mole. Rossini, Wagman, Evans, Levine, and Jaffe [10] give -179.3 kcal/mole for the heat of formation of TiCl_4 at 25°C based also on Thomsen's primary data.

Humphrey [7] has determined the heat of formation of TiO_2 to be -225.7 kcal/mole by combustion in an oxygen bomb. From this value for the heat of formation of TiO_2 , the accepted values [10] for the heats of formation of water and aqueous hydrochloric acid, and the corrected value obtained by Roth and Becker for Thomsen's heat of hydrolysis, the heat of formation of $\text{TiCl}_{4(lq)}$ at 25°C is calculated to be -194.7 kcal/mole. An error of 4 percent in Thomsen's value for the heat of hydrolysis of TiCl_4 could explain the discrepancy between his value and that obtained in the present investigation. In view of the uncertainty in the states of the hydrolysis products, this is highly probable.

Since the completion of this investigation, there have been reported four independent determinations of the heat of formation of titanium tetrachloride.

Farber and Darnell [11] studied the equilibrium:



in the temperature range of 800 to $1,400^\circ\text{K}$. Their data lead to -192.5 ± 0.5 kcal/mole for the heat of formation of liquid TiCl_4 at 25°C .

Skinner and Ruehrwein [12] measured the heat of formation directly by carrying out the reaction of titanium with chlorine under pressure and obtained -190.3 ± 3.0 kcal/mole.

Gross, Hayman, and Levi [13] measured the heat of the reaction of titanium with liquid chlorine and the heat of solution of the tetrachloride in chlorine. Using 4.406 kcal/mole for the heat of vaporization of the chlorine, they obtained -191.5 ± 0.3 kcal/mole for the heat of formation of $\text{TiCl}_{4(lq)}$.

Krieve, Vango, and Mason [14] measured the heats of formation of $\text{TiCl}_{4(lq)}$ by carrying out the reaction of $\text{Ti}_{(s)}$ with $\text{Cl}_{2(gas)}$ under pressure in a nickel bomb. They obtained -190.0 ± 0.4 kcal/mole for the heat of formation under standard conditions.

A comparison of the experimental values is given in the following tabulation:

Farber and Darnell	-192.5 ± 0.5 ,
Skinner and Ruehrwein	-190.3 ± 3.0 ,
Gross, Hayman, and Levi	-191.5 ± 0.3 ,
Krieve, Vango, and Mason	-190.0 ± 0.4 ,
This investigation	-192.3 ± 0.7 .

It should be emphasized that the value obtained in this investigation is independent of the heat of vaporization of chlorine and of any heats of solution which may introduce additional errors.

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